

WHAT IS CLAIMED IS:

1. A stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate having an NCO group content of from 15 to 30% and comprising the reaction product of:

- 5 a)(1) a diphenylmethane diisocyanate comprising:
- (i) from 10 to 40% by weight of 2,4'-diphenylmethane diisocyanate,
  - (ii) from 0 to 6% by weight of 2,2'-diphenylmethane diisocyanate,
  - 10 and
  - (iii) from 54 to 90% by weight of 4,4'-diphenylmethane diisocyanate,

wherein the %'s by weight of a)(1)(i), a)(1)(ii) and a)(1)(iii) total 100% by weight of a)(1);

15 and

- b) an organic compound containing at least one hydroxyl group,

in the presence of a catalytic amount of

- 20 c) at least one catalyst selected from the group consisting of (1) one or more trimer catalysts, (2) one or more allophanate catalysts, (3) an allophanate-trimer catalyst system and (4) mixtures thereof;

25 wherein component b) is present in a quantity such that there are from about 0.01 to about 0.25 equivalent hydroxyl groups per equivalent of isocyanate of the MDI present, at least about 50% of the urethane groups are converted to allophanate groups by c) said catalyst or catalyst system, and a catalyst stopper is added once the desired NCO group content is attained.

2. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein the NCO group content is from 20 to 28%.

5 3. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein a)(1) said diphenylmethane diisocyanate comprises (i) from 20 to 35% by weight of the 2,4'-isomer, (ii) from 0 to 2% by weight of the 2,2'-isomer, and (iii) from 63 to 80% by weight of the 4,4'-isomer, with the %'s by weight of a)(1)(i),  
10 a)(1)(ii) and a)(1)(iii) totaling 100% by weight of a)(1).

4. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein component b) is present in an amount such that there are from about 0.01 to 0.20  
15 equivalent hydroxyl groups per equivalent of isocyanate of the diphenylmethane diisocyanate present.

5. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein at least about 70% of  
20 the urethane groups are converted to allophanate groups by c) said catalyst.

6. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein the allophanate groups  
25 and the trimer groups were formed simultaneously.

7. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein the allophanate groups were formed first, and then the trimer groups were formed.

8. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein b) said organic compound has a molecular weight of from about 32 to about 6,000 and contains from about 1 to about 4 hydroxyl groups.

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9. The stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1, wherein b) comprises 2-propanol or isobutyl alcohol.

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10. A process for the preparation of a stable liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate having an NCO group content of from 15 to 30%, comprising:

(1) heating

a)(1) diphenylmethane diisocyanate comprising:

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(i) from 10 to 40% by weight of 2,4'-diphenylmethane diisocyanate,

(ii) from 0 to 6% by weight of 2,2'-diphenylmethane diisocyanate,

and

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(iii) from 54 to 90% by weight of 4,4'-diphenylmethane diisocyanate,

wherein the %'s by weight of a)(1)(i), a)(1)(ii) and a)(1)(iii) total 100% by weight of a)(1);

and

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b) an organic compound containing at least one hydroxyl group,

to a temperature of about 70 to 120°C for a time period of about 1 to about 6 hrs., in the presence of a catalytic amount of:

c) at least one catalyst selected from the group consisting of (1) one or more trimer catalysts, (2) one or more allophanate catalysts, (3) an allophanate-trimer catalysts system and (4) mixtures thereof;  
5 wherein the quantity of b) is such that there are from about 0.01 to about 0.25 equivalent hydroxyl groups per equivalent of isocyanate of the MDI present, and at least about 50% of the urethane groups are converted to allophanate groups by c) said catalyst(s),

10 and  
(2) adding a catalyst stopper once the desired NCO group content of the reaction mixture in (1) is attained to neutralize the catalyst in the reaction mixture.

15 11. The process of Claim 10, wherein the NCO group content is from 20 to 28%.

12. The process of Claim 10, wherein a)(1) said diphenylmethane diisocyanate comprises (i) from 20 to 35% by weight of  
20 the 2,4'-isomer, (ii) from 0 to 2% by weight of the 2,2'-isomer, and (iii) from 63 to 80% by weight of the 4,4'-isomer, with the %'s by weight of a)(1)(i), a)(1)(ii) and a)(1)(iii) totaling 100% by weight of a)(1).

13. The process of Claim 10, wherein component b) is present  
25 in an amount such that there are from about 0.01 to 0.20 equivalent hydroxyl groups per equivalent of isocyanate of the diphenylmethane diisocyanate present.

14. The process of Claim 10, wherein at least about 70% of the  
30 urethane groups are converted to allophanate groups by c) said catalyst.

15. The process of Claim 10, wherein c) the catalyst is selected such that the allophanate groups and the trimer groups form simultaneously.

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16. The process of Claim 10, wherein c) the catalyst is selected such that the allophanate groups are formed first, and then another suitable catalyst c) is added such that the trimer groups are formed.

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17. The process of Claim 10, wherein b) said organic compound has a molecular weight of from about 32 to about 6,000 and contains from about 1 to about 4 hydroxyl groups.

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18. The process of Claim 10, wherein b) comprises 2-propanol or isobutyl alcohol.

19. A stable liquid allophanate-modified, partially trimerized diphenylmethane diisocyanate having an NCO group content of from 15 to 30% and comprising:

20 (A) from 20 to 65% by weight, based on 100% by weight of (A) and (B), of an allophanate-modified diphenylmethane diisocyanate having an NCO group content of from about 16 to about 29%, and comprising the reaction product of:

25 a)(2) a diphenylmethane diisocyanate comprising  
(i) from 0 to 60 % by weight of 2,4'-diphenylmethane diisocyanate,  
(ii) from 0 to 6% by weight of 2,2'-diphenylmethane diisocyanate,  
and

(iii) from 34 to 100% by weight of 4,4'-diphenylmethane diisocyanate,

wherein the %'s by weight of a)(2)(i), a)(2)(ii) and a)(2)(iii) total 100 % by weight of a)(2);

5 and

b) an organic compound containing at least one hydroxyl group,

in the presence of

c)(2) one or more allophanate catalyst,

10 wherein component b) is present in a quantity such that there are from about 0.05 to about 0.25 equivalent hydroxyl groups per equivalent of isocyanate of the MDI present; at least about 50% of the urethane groups are converted to allophanate groups by c)(2), and a catalyst stopper is added once the desired NCO group  
15 content of the allophanate-modified MDI is attained;

and

(B) from 35 to 80% by weight, based on 100% by weight of (A) and (B), of a partially trimerized diphenylmethane diisocyanate having an NCO group content of from about 20 to about 31%, and comprising  
20 the trimerization product of:

a)(3) a diphenylmethane diisocyanate comprising

(i) from 10 to 60 % by weight of 2,4'-diphenylmethane diisocyanate,

(ii) from 0 to 6% by weight of 2,2'-diphenylmethane diisocyanate,  
25

and

(iii) from 34 to 90% by weight of 4,4'-diphenylmethane diisocyanate,

wherein the %'s by weight of a)(3)(i), a)(3)(ii) and a)(3)(iii)

30 total 100 % by weight of a)(3),

in the presence of

- c) at least one catalyst selected from the group consisting of  
(1) one or more trimer catalysts, (3) a trimer-allophanate  
catalyst system and (4) mixtures thereof;

5 wherein the trimer content is at least about 10 to about 80%, based  
on 100% by weight of component (B), and a catalyst stopper is  
added once the desired NCO group content of the trimer modified  
MDI is attained.

10 20. The blend of Claim 19 having an NCO group content of 20 to  
28%, and comprising:

- (A) from 30 to 60% by weight, based on 100% by weight of (A) and (B),  
of an allophanate-modified diphenylmethane diisocyanate having  
an NCO group content of about 20 to about 28%,

15 and

- (B) from 40 to 70% by weight, based on 100% by weight of (A) and (B),  
of partially trimerized diphenylmethane diisocyanate having an  
NCO group content of about 22 to about 29%

20 21. The blend of Claim 19, wherein:

- (A) said allophanate-modified diphenylmethane diisocyanate  
comprises the reaction product of:

a)(2) a diphenylmethane diisocyanate comprising:

25 (i) from 10 to 50% by weight of 2,4'-diphenylmethane  
diisocyanate,

(ii) from 0 to 4% by weight of 2,2'-diphenylmethane  
diisocyanate,

and

30 (iii) from 50 to 90% by weight of 4,4'-diphenylmethane  
diisocyanate,

with the %'s by weight of a)(2)(i), a)(2)(ii) and a)(2)(iii) totaling 100% by weight of a)(2);

- b) an organic compound having a molecular weight of from about 32 to about 6,000 and containing from about 1 to about 4 hydroxyl groups;

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in the presence of

- c) one or more allophanate catalyst.

22. The blend of Claim 19, wherein in (A) the allophanate-modified diphenylmethane diisocyanate, the quantity of b) is such that there are from about 0.10 to 0.20 equivalent hydroxyl groups per equivalent of isocyanate of the MDI present, and at least about 70% of the urethane groups are converted to allophanate groups.

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23. The blend of Claim 19, wherein (B) said trimerized diphenylmethane diisocyanate comprises the trimerization product of a)(3) a diphenylmethane diisocyanate comprising the reaction product of:

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- (i) from 20 to 40% by weight of 2,4'-diphenylmethane diisocyanate,

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- (ii) from 0 to 2% by weight of 2,2'-diphenylmethane diisocyanate,

and

- (iii) from 60 to 80% by weight of 4,4'-diphenylmethane diisocyanate,

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wherein the %'s by weight of a)(3)(i), a)(3)(ii) and a)(3)(iii) total 100% by weight of a)(3);

in the presence of:

- c) at least one catalyst selected from the group consisting of  
(1) one or more trimer catalysts, (3) a trimer-allophanate  
catalyst system and (4) mixtures thereof;

5 wherein the trimer content is at least about 25 to about 60%, based  
on 100% by weight of component (B).

24. The blend of Claim 19, wherein b) said organic compound  
has a molecular weight of from about 32 to about 6,000 and contains from  
about 1 to about 4 hydroxyl groups.

10 25. The blend of Claim 19, wherein b) comprises 2-propanol or  
isobutyl alcohol.

26. A process for the preparation of a stable liquid allophanate-  
modified, partially trimerized diphenylmethane diisocyanate having an  
15 NCO group content of from 15 to 30% and comprising

(1) blending

- (A) from 20 to 65% by weight, based on 100% by weight of (A)  
and (B), of an allophanate-modified diphenylmethane  
diisocyanate having an NCO group content of from about 16  
20 to about 29, and comprising the reaction product of  
a)(2) a diphenylmethane diisocyanate comprising  
(i) from 0 to 60 % by weight of 2,4'-  
diphenylmethane diisocyanate,  
(ii) from 0 to 6% by weight of 2,2'-  
25 diphenylmethane diisocyanate,  
and  
(iii) from 34 to 100% by weight of 4,4'-  
diphenylmethane diisocyanate,  
wherein the %'s by weight of a)(2)(i), a)(2)(ii)  
30 and a)(2)(iii) total 100 % by weight of a)(2),

with

b) an organic compound containing at least one hydroxyl group,

in the presence of:

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c) (2) one or more allophanate catalyst,

wherein component b) is present in a quantity such that there are from about 0.05 to about 0.25 equivalent hydroxyl groups per equivalent of isocyanate of the MDI present, at least about, at least about 50% of the urethane groups are converted to allophanate groups by c)(2) and a catalyst stopper is added once the desired NCO group content of the allophanate-modified MDI is attained;

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with

(B) from 35 to 80% by weight, based on 100% by weight of (A) and (B), of an at least partially trimerized diphenylmethane diisocyanate having an NCO group content of from about 20 to about 31%, and comprising the trimerization product of a)(3) a diphenylmethane diisocyanate comprising

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(i) from 10 to 60 % by weight of 2,4'-diphenylmethane diisocyanate,

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(ii) from 0 to 6% by weight of 2,2'-diphenylmethane diisocyanate,

and

(iii) from 34 to 90% by weight of 4,4'-diphenylmethane diisocyanate,

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wherein the %'s by weight of a)(3)(i), a)(3)(ii) and a)(3)(iii) total 100% by weight of a)(3),

formed in the presence of:

c) at least one catalyst selected from the group consisting of (1) one or more trimer catalyst, (3) a

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trimer-allophanate catalyst system and (4) mixtures thereof;

wherein the trimer content is at least about 10 to about 80%, based on 100% by weight of component (B), and a catalyst stopper is added once the desired NCO group content is achieved,

and

(2) cooling the blend to ambient temperature.

27. The process of Claim 26, having an NCO group content of 20 to 28%, and comprising:

(A) from 30 to 60% by weight, based on 100% by weight of (A) and (B), of an allophanate-modified diphenylmethane diisocyanate having an NCO group content of about 20 to about 28%,

and

(B) from 40 to 70% by weight, based on 100% by weight of (A) and (B), of partially trimerized diphenylmethane diisocyanate having an NCO group content of about 22 to about 29%

28. The process of Claim 26, wherein:

(A) said allophanate-modified diphenylmethane diisocyanate comprises the reaction product of:

a)(2) a diphenylmethane diisocyanate comprising:

(i) from 10 to 50% by weight of 2,4'-diphenylmethane diisocyanate,

(ii) from 0 to 4% by weight of 2,2'-diphenylmethane diisocyanate,

and

(iii) from 50 to 90% by weight of 4,4'-diphenylmethane diisocyanate,

with the %'s by weight of a)(2)(i), a)(2)(ii) and a)(2)(iii) totaling 100% by weight of a)(2);

- b) an organic compound having a molecular weight of from about 32 to about 6,000 and containing from about 1 to about 4 hydroxyl groups;

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in the presence of

- c) one or more allophanate catalyst.

29. The process of Claim 26, wherein in (A) the allophanate-modified diphenylmethane diisocyanate, the quantity of b) is such that there are from about 0.10 to 0.20 equivalent hydroxyl groups per equivalent of isocyanate of the MDI present, and at least about 70% of the urethane groups are converted to allophanate groups.

15. 30. The process of Claim 26, wherein (B) said trimerized diphenylmethane diisocyanate comprises the trimerization product of a)(3) a diphenylmethane diisocyanate comprising the reaction product of:

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- (i) from 20 to 40% by weight of 2,4'-diphenylmethane diisocyanate,

- (ii) from 0 to 2% by weight of 2,2'-diphenylmethane diisocyanate,

and

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- (iii) from 60 to 80% by weight of 4,4'-diphenylmethane diisocyanate,

wherein the %'s by weight of a)(3)(i), a)(3)(ii) and a)(3)(iii) total 100% by weight of a)(3);

in the presence of:

- c) at least one catalyst selected from the group consisting of  
(1) one or more trimer catalysts, (3) a trimer-allophanate  
catalyst system and (4) mixtures thereof;

5 wherein the trimer content is at least about 25 to about 60%, based  
on 100% by weight of component (B).

31. The process of Claim 26, wherein b) said organic compound  
has a molecular weight of from about 32 to about 6,000 and contains from  
about 1 to about 4 hydroxyl groups.

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32. The process of Claim 26, wherein b) comprises 2-propanol  
or isobutyl alcohol.

33. A storage stable, liquid, urethane prepolymer of an  
15 allophanate modified, partially trimerized diphenylmethane diisocyanate  
having an NCO group content of 8 to 28%, and comprising the reaction  
product of:

- (I) the storage stable, liquid, allophanate-modified, partially trimerized  
diphenylmethane diisocyanate of Claim 1,  
20 and  
(II) an isocyanate-reactive component containing from about 1.5 to  
about 6 hydroxyl groups and having a molecular weight of from  
about 76 to about 10,000.

25 34. The storage stable, liquid, urethane prepolymer of Claim 33,  
wherein the NCO group content is from about 12 to about 26%.

35. The storage stable, liquid urethane prepolymer of Claim 33,  
wherein (II) said isocyanate-reactive component contains from 2 to 6  
30 hydroxyl groups and has a molecular weight of about 90 to about 6,000.

36. A process for the preparation of a storage-stable, liquid, urethane prepolymer of an allophanate-modified, partially trimerized diphenylmethane diisocyanate having an NCO group content of from about 8 to about 28, comprising:

(1) reacting:

(I) the storage stable, liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 1,  
with

(II) an isocyanate-reactive component containing from about 1.5 to about 6 hydroxyl groups and having a molecular weight of from about 76 to about 10,000,  
at a temperature of from 40 to 80°C for 1 to 6 hours.

37. The process of Claim 36, wherein the NCO group content is from about 12 to about 26%.

38. The process of Claim 36, wherein (II) said isocyanate-reactive component contains from 2 to 6 hydroxyl groups and has a molecular weight of about 90 to about 6,000.

39. A storage stable, liquid, urethane prepolymer of an allophanate modified, partially trimerized diphenylmethane diisocyanate having an NCO group content of 8 to 28%, and comprising the reaction product of:

(III) the storage-stable, liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 19,

and

(II) an isocyanate-reactive component containing from about 1.5 to about 6 hydroxyl groups and having a molecular weight of from

about 76 to about 10,000.

40. The prepolymer of Claim 39, wherein the NCO group content is from about 12 to about 26%.

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41. The prepolymer of Claim 39, wherein (II) said isocyanate-reactive component contains from 2 to 6 hydroxyl groups and has a molecular weight of about 90 to about 6,000.

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42. A process for the preparation of a storage-stable, liquid, urethane prepolymer of an allophanate-modified, partially trimerized diphenylmethane diisocyanate having an NCO group content of from about 8 to about 28%, comprising:

(1) reacting:

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(III) the storage-stable, liquid, allophanate-modified, partially trimerized diphenylmethane diisocyanate of Claim 19,  
and

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(II) an isocyanate-reactive component containing from about 1.5 to about 6 hydroxyl groups and having a molecular weight of from about 76 to about 10,000,  
at a temperature of from 40 to 80°C for 1 to 6 hours.

43. The process of Claim 42, wherein the NCO group content is from about 12 to about 26%.

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44. The process of Claim 42, wherein (II) said isocyanate-reactive component contains from 2 to 6 hydroxyl groups and has a molecular weight of about 90 to about 6,000.